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Invention: METHOD OF FORMING UNIFORM ULTRA-THIN OXYNITRIDE LAYERS

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<u>This is a:</u>

☐ Provisional Application

☒ Regular Utility Application

☐ Continuing Application
  ☐ The contents of the parent are incorporated
    by reference

☐ PCT National Phase Application

☐ Design Application

☐ Reissue Application

☐ Plant Application

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  Sub. Spec. filed _____
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SPECIFICATION

METHOD OF FORMING UNIFORM ULTRA-THIN OXYNITRIDE LAYERS

FIELD OF THE INVENTION

[0001] The present invention relates to semiconductor processing, and more particularly, to a method for forming uniform ultra-thin oxynitride layers.

BACKGROUND OF THE INVENTION

[0002] Thin oxide (e.g., SiO_2) and oxynitride (e.g., SiO_xN_y) layers are often used as dielectric layers at the Si surface of an integrated circuit. This is in part because of excellent electrical properties of the oxide and oxynitride layers, including high electron mobility and low electron trap densities. Semiconductor transistor technology is currently requiring oxide and oxynitride gate dielectric layers for conventional gate dielectric applications that are less than about 10-15 angstrom (A) thick, or as thin as 5-7 A for use as interface layers with high-dielectric constant materials (also referred to herein as high-k materials).

[0003] A native oxide layer that is typically a few angstrom thick, forms easily on clean Si surfaces, even at room temperature and atmospheric pressure. An oxide layer with a desired thickness that is larger than the native oxide thickness, can be grown through the native oxide layer, but usually the thickness uniformity and quality of the oxide layer is poor across the entire Si substrate.

[0004] Alternatively, the native oxide (or the chemical oxide) can be removed from a Si surface prior to growing a new oxide layer. The native oxide layer can, for example, be removed using liquid baths containing dilute hydrofluoric acid (HF) or by using HF gas phase etching. A new oxide layer can then be re-grown on the clean Si surface by conventional thermal oxidation, but the initial oxidation can proceed quickly and result in poor thickness uniformity and inadequate electrical properties. For ultra-thin (less than about 20 A) oxide layers used in transistor technologies, the leakage current is dominated by the tunneling current.

[0005] Si-oxynitride layers are viewed as one of the most promising alternate material to replace the SiO_2 gate oxide, while still being compatible with the Si technology. Thin oxynitride layers are usually formed either by thermal processing methods or by plasma-based methods. Nitridation of ultra-thin oxide layers, that results in the formation of oxynitride layers, has been shown to alleviate various limitations encountered with oxide layers. The improvements include increased resistance to boron penetration, lower tunneling leakage current and interface-state generation, and less threshold voltage shift under constant current conditions. The improved dielectric properties that are observed for oxynitride layers are attributed to the fact that the nitrogen atoms at the surface of the SiO_2/Si act as a barrier to boron penetration and can reduce strain at the SiO_2/Si interface.

SUMMARY OF THE INVENTION

[0006] A method is provided for forming ultra-thin oxynitride layers for gate dielectric applications, and other applications, such as dielectric interface layers underneath high-k materials. The method utilizes low partial pressure of a nitrogen-containing oxidizing gas and optionally an oxygen-containing gas, to achieve self-limiting oxidation of substrates that results in ultra-thin oxynitride layers.

[0007] In one embodiment of the invention, a substrate to be processed can be clean and lack an initial dielectric layer. Self-limiting oxidation of the substrate results in formation of an ultra-thin oxynitride layer on the substrate.

[0008] In an alternate embodiment of the invention, the substrate to be processed can contain an initial dielectric layer comprising at least one of an oxide layer, an oxynitride layer, and a nitride layer. The initial dielectric layer is used to control the growth of an ultra-thin oxynitride layer in a self-limiting oxidation of the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] In the drawings:

[0010] FIG. 1A schematically shows a cross-sectional view of a gate electrode microstructure;

[0011] FIG. 1B schematically shows a cross-sectional view of an alternate gate electrode microstructure;

[0012] FIG. 2A shows oxide thickness versus oxidation time for oxide layers grown by a self-limiting process;

[0013] FIG. 2B shows oxide uniformity versus oxidation time for oxide layers grown by a self-limiting process;

[0014] FIG. 3A schematically shows a cross-sectional view of a clean substrate;

[0015] FIG. 3B schematically shows a cross-sectional view of an oxynitride layer grown by a self-limiting process according to an embodiment of the present invention;

[0016] FIG. 4 shows a flowchart for forming an oxynitride layer according to an embodiment of the invention;

[0017] FIG. 5A schematically shows a cross-sectional view of an oxide layer overlying a substrate;

[0018] FIG. 5B schematically shows a cross-sectional view of an oxynitride layer grown by a self-limiting process according to an alternate embodiment of the invention;

[0019] FIG. 6A schematically shows a cross-sectional view of a dielectric layer overlying a substrate;

[0020] FIG. 6B schematically shows a cross-sectional view of an oxynitride layer grown by a self-limiting process according to an alternate embodiment of the invention;

[0021] FIG. 7 shows a flowchart for forming an oxynitride layer according to an alternate embodiment of the invention; and

[0022] FIG. 8 shows a simplified block diagram of a processing system for forming oxynitride layers.

DETAILED DESCRIPTION OF THE INVENTION

[0023] A method is provided for forming ultra-thin oxynitride dielectric layers. The oxynitride layers find use in semiconductor microstructures, for example, as gate dielectrics and as dielectric interface layers located between high-k materials and the underlying substrates.

[0024]   FIG. 1A schematically shows a cross-sectional view of a gate electrode microstructure. The gate electrode microstructure 10, which can be a part of an integrated circuit, comprises a substrate 100, a dielectric layer 102, and an electrode layer 106. The substrate 100 can, for example, be a Si substrate that is single-crystal Si or polycrystalline-Si (poly-Si). A Si substrate can include numerous active devices and/or isolation regions (not shown). A Si substrate 100 can be of n- or p-type, depending on the type of device being formed, and can, for example, consist of a substrate of any diameter, such as a substrate with a diameter greater than about 195 mm, e.g., a 200 mm substrate, a 300 mm substrate, or an even larger substrate. In addition to the traditional doped poly-Si, the electrode layer 106 can, for example, comprise at least one of W, Al, TaN, TaSiN, HfN, HfSiN, TiN, TiSiN, Re, Ru, and SiGe.

[0025]   The dielectric layer 102 overlying the substrate 100 can, for example, comprise at least one of an ultra-thin (less than about 20 A) oxide layer and an oxynitride layer. It should be noted that the term "oxide" includes oxidized materials containing oxygen that are typically used in semiconductor applications. Such materials include, for example, Si, that forms a SiO_2 dielectric layer upon oxidation. An oxide layer can be formed using thermal oxidation of the substrate in the presence of a process gas that comprises an oxygen-containing gas, e.g., O_2, O_3, H_2O, and H_2O_2.

[0026]   The term "oxynitride" includes oxidized materials containing oxygen and nitrogen. Such materials include, for example, Si-oxynitride, that forms SiO_xN_y in an oxidation process that includes nitrogen-incorporation. An oxynitride layer is commonly formed using a process gas comprising a nitrogen-containing oxidizing gas containing at least one of NO, N_2O, and NH_3. For example, high quality SiO_xN_y layers can be formed using rapid thermal nitrous oxide (RTNO) treatment of Si surfaces. Alternatively, oxynitride layers can be formed using plasma nitridation methods, including remote plasma nitridation (RPN) of oxide layers.

[0027]   Nitrogen-content and nitrogen distribution within an oxynitride layer can influence the device performance. Oxynitride layers can have an isotropic distribution of nitrogen and oxygen atoms, or alternatively, the atom distribution can be anisotropic. Nitrogen incorporation into oxide layers is used to increase the dielectric constant of the oxide layers, to control Si

surface oxidation, and to act as a barrier layer to prevent diffusion of atoms through the different layers. Increasing the dielectric constant can reduce the leakage current that is observed when compared to an oxide layer having the same capacitance.

[0028] In current semiconductor devices, one function of gate dielectric layers is to "gate" the electrons, by controlling the flow of electricity across the transistor. With the introduction of high-k materials, these layers will likely still be required at the channel and/or gate electrode to preserve interface state characteristics. This includes forming an interface with good electrical properties, preventing uncontrolled Si surface oxidation, reducing reactions between different layers, and acting as a barrier layer to prevent diffusion of atoms to the different layers (e.g., dopant penetration from the gate electrode 106 into the substrate 100). In practice, in order to achieve good device performance, it is important to control the thickness of the dielectric layer 102, such that it remains thin, thereby avoiding increasing the equivalent oxide thickness (EOT) of the gate electrode microstructure.

[0029] FIG. 1B schematically shows a cross-sectional view of an alternate gate electrode structure. The gate electrode structure 20 in FIG. 1B differs from the gate electrode structure in FIG. 1A by a relatively thick high-k layer 104 that is located between the electrode layer 106 and the dielectric layer 102. Dielectric materials featuring a dielectric constant greater than that of SiO_2 (k~3.9) are commonly referred to as high-k materials. In addition, high-k materials may refer to dielectric materials that are deposited onto substrates rather than grown on the surface of the substrate (e.g., SiO_2, SiO_xN_y). The high-k layer can, for example, be selected from one of HfO_2, ZrO_2, Ta_2O_5, TiO_2, Al_2O_3, and HfSiO. The high-k layer 104 in the gate electrode structure 20 can be physically thicker than the dielectric layer 102, while attaining the necessary capacitance.

[0030] Semiconductor transistor technology is currently requiring oxide and oxynitride layers that are less than about 10-15 A thick for conventional gate dielectric applications (FIG. 1A), or as thin as about 5-7 A for use as dielectric interface layers with high-k materials (FIG. 1B). In order to form ultra-thin oxynitride layers that are thinner (less than about 10 A) than an initial dielectric layer (e.g., an oxide layer, an oxynitride layer, or a nitride layer), can

require removal of at least a portion of the initial dielectric layer prior to growing the oxynitride layers.

[0031] FIG. 3A schematically shows a cross-sectional view of a clean substrate. A clean substrate is a substrate that does not have an oxide layer or an oxynitride layer. A substrate can be cleaned, for example, by placing it in a liquid bath containing dilute hydrofluoric acid (HF) or, alternatively, exposing it to HF gas phase etching. The dilute HF liquid solution can be a $H_2O:HF$ (e.g., about 50:1) mixture. Following the HF cleaning process, the substrate can be rinsed in de-ionized (D.I.) water prior to the oxidation process.

[0032] FIG. 3B schematically shows a cross-sectional view of an oxynitride layer grown by a self-limiting process according to an embodiment of the present invention. The oxynitride layer 102B has a well-controlled thickness D_{2B} that is uniform over the whole substrate 100. The ultra-thin oxynitride layer can be grown on the clean substrate 100 by a self-limiting process, where the oxynitride growth rate (and the resulting final oxynitride layer thickness) is carefully controlled by selecting the process conditions, particularly the partial pressures of a nitrogen-containing oxidizing gas in the process gas and in the process chamber, and the substrate temperature.

[0033] In the self-limiting process, the process gas can comprise a nitrogen-containing oxidizing gas containing at least one of NO, N_2O, and NH_3. In addition, the process gas can also contain an oxygen-containing gas (e.g., at least one of O_2, O_3, H_2O, and H_2O_2.). Following the formation of an oxynitride layer, the oxynitride layer can be post-annealed using a process gas comprising N_2O or O_2, for example. Alternatively, the oxynitride layer can be post-treated in a plasma nitridation process using a process gas comprising at least one of N_2, NO, N_2O, and NH_3.

[0034] Suitable process conditions that enable self-limiting growth of an oxynitride layer with a desired thickness and thickness uniformity, can be determined by direct experimentation and/or design of experiments (DOE). For example, adjustable process parameters can comprise time, temperature (e.g., substrate temperature), process pressure, and composition of the process gas.

[0035] FIG. 4 shows a flowchart for forming an oxynitride layer according to an embodiment of the invention. At 200, the process is started. At 202, a substrate is positioned in a process chamber and the chamber is evacuated. At 204, a process gas comprising a nitrogen-containing oxidizing gas (e.g., NO N_2O, or NH_3), and optionally an oxygen-containing gas (e.g., O_2, O_3, H_2O, and H_2O_2), is flowed into the process chamber. At 206, an oxynitride layer is formed on the substrate in a self-limiting oxidation process. The substrate is processed for a time period that enables formation of the desired oxynitride layer, and the process ends at 208.

[0036] FIG. 5A schematically shows a cross-sectional view of an oxide layer overlying a substrate. The initial oxide layer 102C has a thickness D_{2C} and can, for example, be an ultra-thin native oxide layer that is typically a few angstrom thick, and forms easily on surfaces of various clean substrates (e.g., Si), even at room temperature and atmospheric pressure. Alternatively, the initial oxide layer 102C can be a chemically deposited oxide layer formed by a self-limiting oxidation process. The initial oxide layer 102C can provide a starting growth layer for growing a thicker oxynitride layer with good thickness control and thickness uniformity.

[0037] FIG. 5B schematically shows a cross-sectional view of an oxynitride layer grown by a self-limiting process according to an alternate embodiment of the invention. The thickness D_{2C} of the oxide layer 102C in FIG. 5A is less than the thickness D_{2D} of the oxynitride layer 102D. Importantly, due to the self-limiting growth mechanism of the oxynitride layer 102D, it is not necessary for the initial oxide layer 102C to have good thickness uniformity, in order to grow an oxynitride layer 102D with good thickness uniformity.

[0038] FIG. 6A schematically shows a cross-sectional view of a dielectric layer overlying a substrate. The initial dielectric layer 102E can, for example, be an oxynitride layer or a nitride layer that is a few angstrom thick (D_{2E}). FIG. 6B schematically shows a cross-sectional view of an oxynitride layer 102F grown by a self-limiting process according to another embodiment of the invention. The initial oxynitride or nitride layer 102E in FIG. 6A is used to control the growth of an oxynitride layer 102F at the Si interface, where the thickness D_{2F} of the oxynitride layer 102F is controlled by a self-limiting reaction of the substrate through the dielectric layer 102E. The resulting

oxynitride layer 102F contains oxidized material from the reaction of the oxidizing species with the substrate 100 and with the dielectric layer 102E. The initial dielectric layer 102E, itself, can be formed in a self-limiting oxidation process.

[0039] FIG. 7 shows a flowchart for forming an oxynitride layer according to an alternate embodiment of the invention. At 210, the process is started. At 212, a substrate containing an initial dielectric layer is positioned in a process chamber and the chamber is evacuated. The initial dielectric layer can comprise at least one of an oxide layer, an oxynitride layer, or a nitride layer. A nitride layer can, for example, comprise a SiN_x layer, formed using deposition of a SiN_x material or nitridation of a Si layer. At 214, a process gas comprising a nitrogen-containing oxidizing gas and optionally an oxygen-containing gas, is flowed into the process chamber. At 216, an oxynitride layer is formed in self-limiting oxidation of the substrate. The substrate is processed for a time period that enables formation of the desired oxynitride layer, and the process ends at 218.

[0040] FIG. 2A shows oxide thickness versus oxidation time for oxide layers grown by a self-limiting process. The starting 200 mm Si substrates (wafers) in FIG. 2A, contained chemical oxide layers that were about 10A thick. Self-limiting oxidation of the Si substrates containing the chemical oxide layers was carried out for 3 to 80 min under low-pressure conditions. The oxidation process utilized a process gas containing an about 3:1 $N_2:O_2$ gas mixture, a process chamber pressure of about 8 Torr, and a substrate temperature of about 700° C. Typical gas flows were about 3 slm N_2 and about 1 slm O_2 in a batch type process chamber for a 100 wafer batch of 200 mm wafers.

[0041] The oxidation curves in FIG. 2A show the average oxide thickness measured at 9 points (lower curve) and 49 points (upper curve) on the substrates using ellipsometry and a refraction index of 1.46. It is evident from FIG. 2A that the oxide growth saturates at an oxide thickness of about 15 A. At each measured oxidation time (3, 10, 45, 80min), the oxide layer thickness varied by less than about 1 A for all 49 measurement points.

[0042] FIG. 2B shows oxide uniformity versus oxidation time for oxide layers grown by a self-limiting process. The oxide thickness uniformity for the 9

point and 49 point measurements is shown as %3-sigma values, and the overall trend shows improved oxide thickness uniformity over the whole Si substrate as the oxide layers grow thicker. Electrical measurements obtained for ultra-thin oxide layers (~15 A) shown in FIGs. 2A and 2B, showed good electrical properties when used as interface layers underneath high-k layers in gate electrode microstructures (see FIG.1B).

[0043] The basic mechanism in a dry oxidation process is the diffusion of an oxidizing species through an existing dielectric layer (e.g., oxide, oxynitride, or nitride layer) and the reaction of the oxidizing species with the substrate at the oxide/substrate interface. In a self-limiting oxidation process, the rate of oxidation decreases as the thickness of the dielectric layer increases. This is likely due to hindered diffusion of the oxidizing species through the existing layer to the layer/substrate interface.

[0044] In mathematical terms, Fick's Law ($J=-D \times dC/dx$) describes the dependence of mass flux (J) through a layer, on the ratio of change in concentration (dC) to the change in layer thickness (dx), with a material constant diffusivity (D). The partial pressure of the oxidizing ambient is used to control the concentration gradient component, which in turn determines the final thickness of the layer given a fixed mass flux, which is at the limit of the oxidation potential (self-limited oxidation). In order to achieve properties of self-limiting oxidation, it is important that the oxidation ambient forms an oxidation barrier on the substrate. In FIG. 2A, only about 0.5 A of additional oxide growth is observed during the last 30 min of the 80 min self-limited process, and the self-limiting process leads to a more uniform oxide layer thickness.

[0045] In the self-limiting oxidation process, FIGs. 2A and 2B illustrate that substrate regions that contain a relatively thin oxide layer, grow slower than regions where the oxide layer is thicker. This leads to formation of oxide layers where the thickness of the oxide layer is uniform over the whole substrate, whether the initial oxide layer is uniform or not. We believe that the slow oxide growth rate that is observed in FIGs. 2A and 2B, advantageously permits long oxidation/anneal times, and improves the electrical quality of the

resulting oxide layer, by removing bulk and interface traps, when a saturated, fully oxidized, stable oxide layer is formed.

[0046] In a self-limiting oxidation process for forming oxynitride layers, the oxynitride growth rate (and the resulting final oxynitride layer thickness) can be reduced/increased by decreasing/increasing the partial pressure of the nitrogen-containing oxidizing gas in the process chamber. A low partial pressure of the nitrogen-containing oxidizing gas allows controlled growth of thin oxynitride layers. The partial pressure of the nitrogen-containing oxidizing gas can, for example, be less than about 10 Torr. In an alternate embodiment, the partial pressure of the nitrogen-containing oxidizing gas can be less than about 5Torr. In addition, the growth rate of the oxynitride layer can be reduced/increased by lowering/increasing the substrate temperature. The pressure of the processing chamber can be less than atmospheric pressure. Alternatively, the process chamber pressure can be less than about 50 Torr.

[0047] The oxidation data whose results are illustrated in FIGs. 2A and 2B, illustrates that it is possible to reproducibly grow oxide layers that are about 15 A thick, with excellent uniformity, from substrates containing oxide layers that are a few angstrom thick. The ability to start with substrates that contain an initial oxide layer (e.g., a chemical or native oxide), can remove the need to strip the initial oxide layer, prior to growing an oxynitride layer on a clean substrate, as long as the initial oxide thickness is less than the desired final oxynitride thickness.

[0048] In the aforementioned process example described in FIGs. 2A and 2B, the process gas comprised O_2 gas and N_2 inert gas. In a self-limiting process to grow oxynitride layers the nitrogen-containing oxidizing gas in process gas can, for example, comprise at least one of NO, N_2O, and NH_3. In addition, the process gas can further contain an oxygen-containing gas (e.g., at least one of O_2, O_3, H_2O, and H_2O_2). Furthermore, the process gas can contain an inert gas. The inert gas can comprise at least one of Ar, He, Ne, Kr, Xe, and N_2. The addition of an inert gas to the process chemistry is, for example, to dilute the process gas or adjust the process gas partial pressure(s).

[0049]   The parameter space for the oxidation process can, for example, utilize a process gas flow rate less than about 2000 sccm, an inert gas flow rate less than about 1000 sccm, and a substrate temperature from about 500° C to about 1000° C. For example, the substrate temperature can be about 700° C. A partial pressure of a nitrogen-containing oxidizing gas can, for example, be less than about 10 Torr. In an alternate embodiment, the partial pressure of a nitrogen-containing oxidizing gas can be less than about 5 Torr. The substrate temperature can be held constant during the oxidation process or, alternatively, the substrate temperature can be ramped during the process. The chamber pressure can be below atmospheric pressure. Alternatively, the chamber pressure can be less than 50 Torr.

[0050]   A processing system for forming ultra-thin oxynitride layers can comprise a batch type process chamber capable of processing multiple substrates (wafers) simultaneously. Alternatively, the processing system can comprise a single wafer process chamber. The process chamber can process substrates of any diameter, such as substrates having a diameter greater than about 195 mm, e.g., 200 mm substrates, 300 mm substrates, or even larger substrates. A batch type process chamber can provide an advantage over single wafer process chambers by allowing long processing times for self-limiting processes.

[0051]   FIG. 8 shows a simplified block diagram of a processing system for forming oxynitride layers. The batch type processing system 300 comprises a process chamber 302, a gas injection system 304, a vacuum pumping system 306, a process monitoring system 308, and a controller 310. The gas injection system 304 is used to introduce a process gas for purging and processing the substrates 306. Multiple substrates 314 can be loaded into the process chamber 302 and processed using substrate holder 312.

[0052]   When carrying out a self-limiting process, it can be advantageous to load the substrates (wafers) to be processed into a process chamber 302 that is at a temperature below which wafer oxidation occurs. A typical process according to the invention can comprise loading the wafers to be processed into a batch type process chamber that is at a temperature of about 300° C and comprises an ambient containing about 1% oxygen. These process

conditions are effective in removing organic contamination from the substrates. In addition, several pump/purge cycles can be performed using an inert gas. Next, the process chamber temperature and process chamber pressure are adjusted to the desired values in an inert ambient to avoid substrate oxidation under non-equilibrium conditions. When the process temperature is reached, the substrates are exposed to a process gas for a time period that results in formation of the desired oxynitride layer. At the end of the oxidation process, the process chamber can be evacuated and purged with an inert gas, and the substrates removed from the process chamber.

[0053] The process can be controlled by a controller 310 capable of generating control voltages sufficient to communicate and activate inputs of the processing system 300 as well as monitor outputs from the processing system 300. Moreover, the controller 310 can be coupled to and exchange information with process chamber 302, gas injection system 304, process monitoring system 308, and vacuum pumping system 306. For example, a program stored in the memory of the controller 310 can be utilized to control the aforementioned components of the processing system 300 according to a stored process recipe. One example of controller 310 is a DELL PRECISION WORKSTATION 610™, available from Dell Corporation, Dallas, Texas.

[0054] Real-time process monitoring can be carried out using process monitoring system 308 during processing. For example, mass spectroscopy (MS) can provide qualitative and quantitative analysis of the gaseous chemical species in the process environment. Process parameters that can be monitored using MS include gas flows, gas pressure, ratios of gaseous species, and gas purities. These parameters can be correlated with prior process results and various physical properties of the oxynitride layers.

[0055] It should be understood that various modifications and variations of the present invention may be employed in practicing the invention. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.